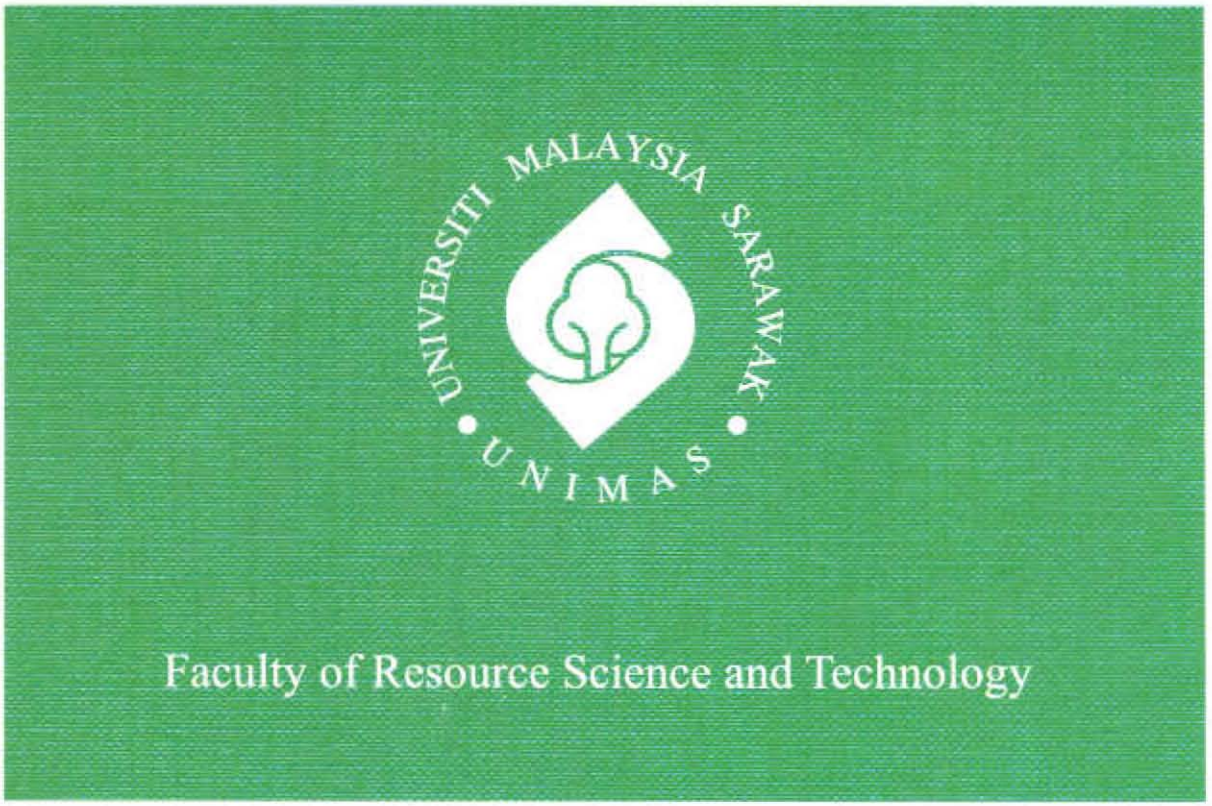

MODIFICATION OF α,β-CONJUGATED ENOL-KETO CONTAINING COMPOUND TOWARDS TO THE SYNTHESIS OF ETHYLENEIMINE COMPOUND AND ITS COMPLEXES

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Bachelor of Science with Honours
(Resource Chemistry)
2012

UNIVERSITI MALAYSIA SAWARAK

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Final Year Project Report ☑

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Modification of α,β-conjugated enol-keto containing compound towards to the synthesis of ethyleneimine compound and its complexes with Co(II)

Ong Cheng Guan (24798)

A dissertation submitted in fulfilment of the requirement for the degree of Bachelor of Science (Hons.)

Resource Chemistry
Department of Chemistry
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2012

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Table of Content

List of Abbreviations I

List of Figures II

List of Tables V

List of Schemes VI

Abstract 1

1.0 Introduction 2

1.1 Schiff Base 2

1.2 Transition Metal 4

1.2.1 Catalysis application 5

1.2.2 Luminescent application 7

1.2.3 Solar energy and electrochemical sensor application 10

1.3 Project overview 12

2.0 Objective 13

3.0 Literature review 14

3.1 Catalytic Dehydrogenation 14

3.2 Synthesis of 2-phenylpyridine 15

3.2.1 Condensation reaction 15

3.2.2 Molecular sieve catalyst 16

3.3 Claisen-Schmidt Condensation 17

3.4 Synthesis of Imines 19

3.4.1 Modification of Stephen reaction 19

3.4.2 Microwave Assisted reaction 20

3.5 Synthesis of cyclometalated octhedral of Co^{3+}, Ir^{3+}, Rh^{3+} complexes 21

3.6 Luminescent Properties of the Group IX transition metal complexes 23

4.0 Methodology 27

4.1 Reagents and materials 27

4.2 Characterization 27

4.3 Preparation of propenal 28

4.4 Preparation of allylidene-(R) 28

4.4.1 Preparation of allylideneamine 28

4.4.2 Preparation of allylidene-4-methylbenzenamine 29

4.5 Preparation of 1,6-Bis-(R)-hexa-2,4-dienedial 29

4.5.1 Preparation of 2,5-dimethyl-hexa-2,4-dienedial 29

4.5.2 Preparation of 1,6-Bis-(phenyl)-hexa-2,4-diene-1,6-dione 30

4.5.3 Preparation of 1,6-Bis-(4-nitro-phenyl)-hexa-2,4-diene-1,6-dione 30

4.6 Preparation of 1,6-Bis-(R)-hexa-2,4-diene-1,6-diamine-2-phenol 31

4.6.1 Attempted preparation of 2,5-Bis-methyl-hexa-2,4-diene-1,6-diamine-2-phenol 31

4.6.2 Attempted preparation of 1,6-Bis-(phenyl)-hexa-2,4-diene-1,6-diamine-2-phenol 32

4.6.3 Preparation of 1,6-Bis-(4-nitro-phenyl)-hexa-2,4-diene-1,6-diamine-2-phenol 32

4.7 Preparation of Co(II) with S Series 33

4.7.1 Preparation of Co(II) with S4 (CS1) 33

4.7.2 Preparation of Co(II) with S3 (CS3) 33

5.0 Results 34

5.1 Allylidene-(R) compounds 34

5.2 Cross-Aldol condensation (L series) compounds 35

5.3 Schiff Bases (S series) compounds 36

5.4 Complexes 37

6.0 Discussion 38

6.1 Synthesis of allylidene-(R) compounds 38

6.1.1 Dehydrogenation of propanal 38

6.1.2 Synthesis of allylideneamine 40

6.1.3 Synthesis of *p*-toluidineallylideneamine 41

6.2 Modification of allylideamine 43

6.2.1 Crossed Aldol-Condensation Reaction, Synthesis and Characterization of L series compounds 45

6.2.1.1 Formation of 2,5(R)-hexa-2,4-dienedial 45

6.2.1.2 Formation of 1,6-Bis-(R)-hexa-2,4-diene-1,6-dione 50

6.2.1.2.A. Infrared analysis 51

6.2.1.2.B. ^{1}H NMR analysis 54

6.2.1.2.C. UV-Vis analysis 56

6.2.2 Synthesis and Characterization of S series compounds 58

6.2.2.1 Formation of (R)-hexa-2,4-diene-1,6-diamine-2-phenol 59

6.2.2.1.A Infrared analysis 60

6.2.2.1.B. Gas chromatography mass spectrum analysis 63

6.2.2.1.C. ^{1}H NMR analysis 65

6.2.2.1.D. UV-visible analysis 69

6.3 Synthesis and characterization of cobalt metal with S series 71

6.3.A Infrared analysis 72

6.3.B UV-visible analysis 76

6.3.C Molar conductivity 77

7.0 Conclusion 78

8.0 Suggestion for future works 79

9.0 References 80

10.0 Appendix 85

List of Abbreviation

$[Ir(ppy)_3]$ = Tris(2-phenylpyridine) iridium(III)

$[Ir(thpy)_3]$ = Tris[2-(2-thionly)pyridine] iridium(III)

$[Rh(bpy)_3]^{3+}$ = Tris(bipyridine) rhodium(III) trication

$[Rh(phen)_3]^{3+}$ = Tris(1,10-phenanthroline) rhodium(III) trication

$[Rh(ppy)_3]$ = Tris(2-phenylpyridine) rhodium(III)

acac = Acetylacetone

bpy = 2,2-Bipyridine

CT = Charge transfer

en = ethlyenediamine

HOMO = highest occupied molecular orbital

ISC = intersystem crossing

LC = ligand centred

LUMO = lowest unoccupied molecular orbital

MLCT = metal to ligand charge-transfer

OLED = organic light emitting diode

phen = 1,10-phenanthroline

ppy = 2-phenylpyridine

thpy = 2-(2-thionly)pyridine

List of Figure

Figure		Page
Figure 1	The basic structure of Schiff base	2
Figure 2	The structure of ruthenium(II) complex	6
Figure 3	The structure of BINOL and BINAM	6
Figure 4	The structure of MDPP and CBP act as donor and host material	7
Figure 5	The structure of *fac*-[Ir(ppy)$_3$]	8
Figure 6	Structure of Schiff base complexes derived from calixarene	9
Figure 7	Structure of bis-[salicylidene-(4-dimethylamino)-aniline] zinc(II)	10
Figure 8	Structure of *N*,*N*'-bis(salicylidene)ethylenediamine zinc(II) iodine	10
Figure 9	Structure of novel chlorine selective membrane Schiff base sensor	11
Figure 10	Structure of *N*,*N*-bis-(salicylidene)-1,2-cyclohexanediamine	11
Figure 11	Structure of [Ir(ppy)$_3$] and [Ru(bpy)$_3$]	12
Figure 12	Structure of [Ir(tpy)$_2$]$^{3+}$	22
Figure 13	The structure of thpy and ppy.	22
Figure 14	Structure of *fac*-[Ir(thpy)$_3$]	23
Figure 15	Structure of ethlyenediamine and 2,2-bipyridine.	24
Figure 16	Structure of [Rh(ppy)$_3$] and [Rh(bpy)$_3$]$^{3+}$	24
Figure 17	Structure of [Rh(phen)$_3$]$^{3+}$	26
Figure 18	IR spectrum of propenal	39

Figure 19 IR septrum of *p*-toluidineallylideneamine 42

Figure 20 Modification containing propenal (basic structure) with different substitution 43

Figure 21 Modification containing allylideneamine (basic structure) with different substitution 44

Figure 22 IR spectrum of 2,5-dimethly-hexa-2,4-dienedial 48

Figure 23 ^{1}H NMR spectrum of 2,5-dimethly-hexa-2,4-dienedial 49

Figure 24 The structure of 1,6-Bis-(R)-hexa-2,4-diene-1,6-dione 50

Figure 25 IR spectrum of 1,6-Bis-(4-nitro-phenyl)-hexa-2,4-diene-1,6-dione 53

Figure 26 ^{1}H NMR spectrum of 1,6-Bis-(4-nitrophenyl)-hexa-2,4-diene-1,6-dione 55

Figure 27 UV-visible spectra of the L series compounds 57

Figure 28 TLC result under UV light of the solid and oil form from the S2 reaction 59

Figure 29 IR spectrum of 2,5-Bis-methly-hexa-2,4-diene-1,6-diamine-2-phenol 61

Figure 30 IR spectrum of 1,6-Bis-(4-nitro-phenyl)-hexa-2,4-diene-1,6-diamine-2-phenol 62

Figure 31 Gas chromatography (top) and mass spectrum (bottom) of S1 63

Figure 32 ^{1}H NMR spectrum of 1,2-ethamine-2-phenol 67

Figure 33 ^{1}H NMR spectrum of 1,6-Bis-(4-nitro-phenyl)-hexa-2,4-diene-1,6-diamine-2-phenol 68

Figure 34 UV-visible spectra of the S series compounds 70

Figure 35 The possible donation points in the modification of Schiff base 71

Figure 36 IR spectrum of CS1 74

Figure 37 IR spectrum of CS3 75

Figure 38 UV-visible spectra of the complexes 76

Figure 39 Suggested pathway of adol-condensation (a) and allylideamine moiety (b) 79

Figure 40 The proposed Schiff base related compounds for future work 79

List of Table

Table		Page
Table 1	Infrared band (cm^{-1}) of each functional group in L series compounds	51
Table 2	^{1}H NMR spectrum of 1,6-Bis-(R)-hexa-2,4-diene-1,6-dione	54
Table 3	Infrared data (cm^{-1}) of (R)-hexa-2,4-diene-1,6-diamine-2-phenol	60
Table 4	^{1}H NMR spectra of 1,2-ethamide-2-phenol	65
Table 5	^{1}H NMR spectra of 1,6-Bis-(4-nitro-phenyl)-hexa-2,4-diene-1,6-diamine-2-phenol (S3)	66
Table 6	IR spectrum (cm^{-1}) of the Cobalt metal complexation	72
Table 7	Molar conductance values of S series Co(II) complexes	77

List of Scheme

Scheme		Page
Scheme 1	The organic Schiff base arylhyrazones	3
Scheme 2	Tautomeric structures of 1, 2, 4-triazole Schiff base	3
Scheme 3	General C-P(O) bond forming reaction mediated by metal.	5
Scheme 4	Modification of phenylpyridine to allylideneamine	12
Scheme 5	Proposed pathway of allylideneamine synthesis	13
Scheme 6	Formation of Schiff base	13
Scheme 7	Synthetic route of aromatization of 3-hydroxy-5-methylcyclohex-2-enone	14
Scheme 8	Synthetic route of ppyH by using lithium	15
Scheme 9	A plausible reaction mechanism for the synthesis of 2-phenylpyridine from acetophenone, ethanol, formaldehyde and ammonia over molecular sieve catalysts	16
Scheme 10	Mechanism of Claisen-Schmidt condensation reaction in the presence of base	17
Scheme 11	Formation of chalcone by using Suzuki reaction	18
Scheme 12	Synthesis of aldimine from aldehyde	19
Scheme 13	Differences between Conventional and Microwave method	20
Scheme 14	Structure of dimer complexes to $[Ir(dpq)_2acac]$ complexes	21
Scheme 15	Formation of hemiaminal and imine	40
Scheme 16	Mechanism of imine formation	41
Scheme 17	Proposed pathway of allylideneamine synthesis	43

Scheme 18 Reaction of cross aldol-condensation reaction 45

Scheme 19 Mechanism of L1 formation via cross aldol-condensation reaction 46

Scheme 20 Self attack mechanism of propanal to yield the by-product 46

Scheme 21 Mechanism of 1,6-Bis-(R)-hexa-2,4-diene-1,6-dione 51

Scheme 22 Tautomerisation of C=C and C=O 52

Scheme 23 The mechanism of S series compounds synthesis 58

Scheme 24 Mass fragmentation of 1,2-ethamide-2-phenol 64

Modification of α,β-conjugated enol-keto containing compound towards to the synthesis of ethyleneimine compound and its complexes with Co(II)

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ABSTRACT:

This project was aimed to synthesize the allylideneamine moiety ligand in order to replace the phenylpyridine (ppy) moiety ligand in the metallacycle complexes. The L series compounds were synthesized by reacting *p*-(R)-acetophenone (R = H or NO_2) to glyoxal through cross-adol condensation reaction. Then, three S series compounds were synthesized by adding 2-aminophenol into the L series compounds using Schiff base synthesis reaction. Two of the S series compounds namely S1 and S2 were not obtained in the synthesis; indeed, another product namely S4 was obtained from the reaction of remaining glyoxal and 2-aminophenol. Two Co^{2+} complexes were prepared from the reaction of respective S4 and S3 compounds to $CoCl_2$ at room temperature and the spectroscopic data from NMR, IR and UV were obtained. There are some changes found in the IR, ^{1}H NMR and UV-visible spectra of complexes compared to their free ligand. The conductivity studies showed that the oxidation states of the complexes were remained at +2 oxidation state and all complexes are neutral complex.

Keywords: Cobalt(II) complexes, allylideneamine.

ABSTRAK:

Projek ini bertujuan untuk mensintesis ligan allylideneamine untuk menggantikan ligan phenylpyridine (ppy) di dalam kompleks kitaran logam. Sebatian siri L telah disintesis melalui tindak balas p-(R)-acetophenone (R = H atau NO2) dengan glyoxal melalui tindak balas pemeluwapan rentas adol. Kemudian, tiga sebatian siri S telah disintesis dengan menambah 2-aminophenol ke dalam sebatian siri L dengan menggunakan tindak balas sintesis asas Schiff bes. Dua sebatian dalam siri S iaitu S1 dan S2 tidak diperolehi dalam sintesis; akan tetapi produk lain iaitu S4 telah diperolehi daripada tindak balas saki-baki glyoxal dengan 2-aminophenol. Dua Co^{2+} *kompleks telah disistesis daripada tindak balas sebatian S4 dan S3 dengan* $CoCl_2$ *pada suhu bilik dan data spektroskopi dari NMR, IR dan UV telah diperolehi. Terdapat beberapa perubahan didalam spektrum IR,* ^{1}*H NMR dan UV-visible kelihatan di kompleks berbanding dengan ligan bebas masing-masing. Kajian kekonduksian menunjukkan bahawa keadaan pengoksidaan kompleks telah kekal pada keadaan pengoksidaan +2 dan semua kompleks adalah neutral.*

Kata Kunci: Kompleks Cobalt(II), allylideneamine.

1.0 INTRODUCTION

1.1 Schiff Base

Schiff base was first reported by Hugo Schiff in 1864. Schiff base can be prepared by condensation of carbonyl compound and amines in different condition with the elimination of water molecules.

The common structural feature of these compounds azomethine group with the general formula RHC=N-R', where R and R' are alky, aryl, cyclo alkyl or heterocyclic group which maybe variously substituted.

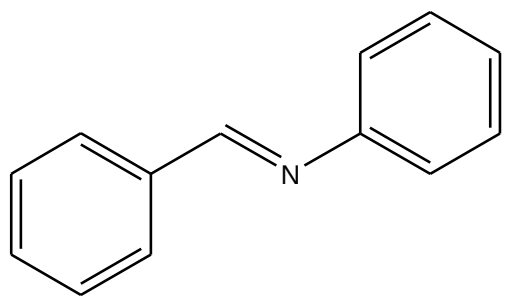
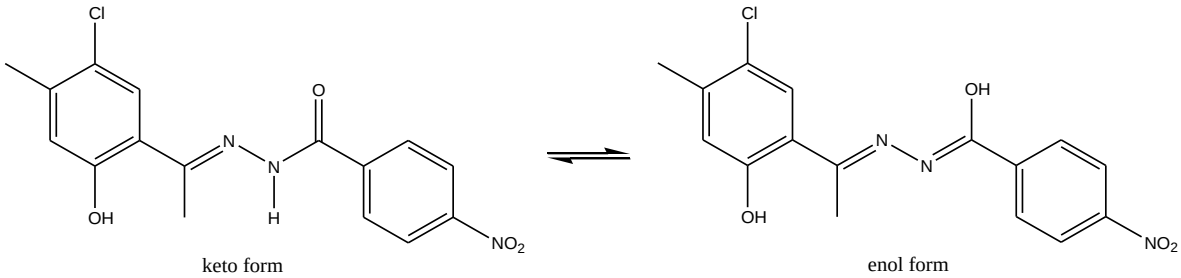


Figure 1: The basic structure of Schiff base

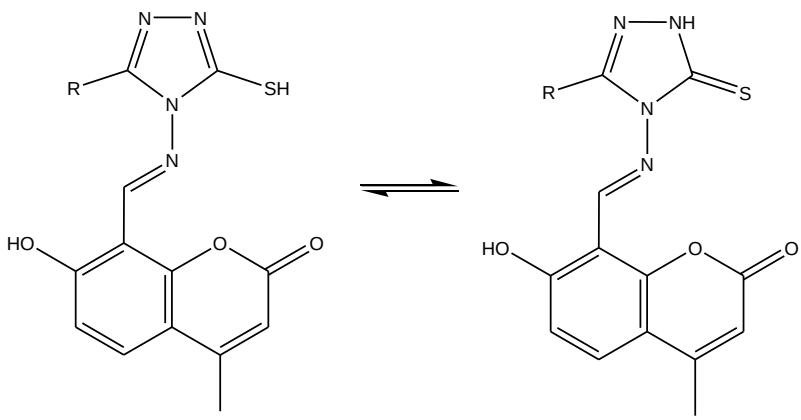
The chelating ability of the Schiff bases combination with ease of preparation and flexibility in varying the chemical environment about the C=N group (imines) make it as an interesting ligand in the coordination chemistry, and as a result, Schiff base is one of the most common ligand in inorganic complexes.

In addition of the complexation studies, Schiff bases containing compounds also have been widely used in different type of applications especially biological and electronic applications. Yaul *et al*. (2009) reported that organic Schiff base arylhyrazones (**Scheme 1**) can be served as the models of biological application as it showed excellent properties in anti-tuberculosis, antimicrobial and corrosion inhibitors.



Scheme 1: The organic Schiff base arylhyrazones by Yaul *et al*. (2009)

Apart from the Schiff bases itself, Schiff base complexes (**Scheme 2**) showed potent antibacterial activity against *Escherichia coli, Staphyococcus aureus, Streptococcus pyogenes, Psedomonas aeruginosa* and *Salmonella typhi* and antifungal activities against *Aspergillus niger, Aspergillus flavus* and *Cladosporium* (Bagihalli *et al*., 2008).



R= H, CH_3, C_2H_5, C_3H_7

Scheme 2: Tautomeric structures of 1, 2, 4-triazole Schiff base by Bagihalli *et al*. (2008)

In 1997, Ming *et al*. reported that Schiff bases have a wide potentially in the electronic application such as in optical information storage and photo-switching due to the fact that it has high chemical stability, high selectivity, sensitivity characteristics and would not be decomposed under UV light irradiation.

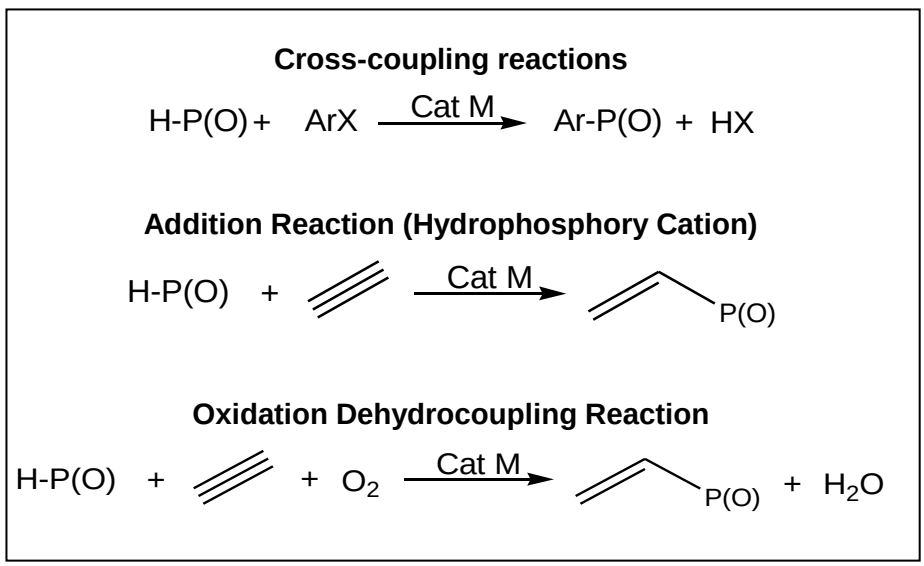
1.2 Transition Metal

Transition metal contains incomplete *d* sub-shells in their electron orbitals which refer to those elements located at group III until XI in the periodic table.

In general, the complexes in the early first row of transition metals namely from Sc to Mn usually have high spin configuration at the ground state, whereas the late transition metal complexes namely Fe to Cu usually have low spin configuration at the ground states (Xu & Han, 2011). The early transition metals (Sc, Ti, V, Cr, Mn) are more basic, because they tend to donate their valence electrons compare to late transition metal (Fe, Co, Ni & Cu) which are more acidic because they prefer to accept electrons in their *d* valance orbitals. Due to this reason, transition metal can exhibit a wide range of oxidation states. Early transition metal can lose their entire *d* valance electrons and give high oxidation state cations such as Cr^{6+} and Mn^{7+}, while late transition metals can only give up to +3 oxidation state. Different oxidation states in between late and early transition metals leads to the different kinds of coordination complexes formed. In general, the early transition metals can form the complexes with higher coordination numbers than those late transition metals. This is due to the various number of oxidation states in transition metals, there are numbers of unique properties in the transition metals which are not found in other elements, for example, colour of the compound and their electronic transferring. As a result, transition metal containing complexes are widely used in the applications such as catalysis, luminescent devices and solar cell properties due to their electron transferring properties in the complex.

1.2.1 Catalysis application

Catalysis is the most early application examples of transition metal containing compounds. The principle of catalysis involves the changing of oxidation states and coordination numbers of the metal centre, which enables the incoming additional ligands interact with the exciting ligands and leave the complex as a new organic product, at the same time, the metal return back to the active catalyst condition and repeat the catalytic process. For example, metal-catalyzed cross coupling reactions of H-P(O) bond with aryl and vinly halides or metal-mediated addition (**Scheme 3**) are potentially of bond formation oxidative dehydrocoupling of H-P(O) bonds with alkynes (Xu & Han, 2011).



Scheme 3: General C-P(O) bond forming reaction mediated by metal

Indeed, Schiff bases containing metal complexes were found, have also been used in the catalysis application. In 1999, Katsuki and co-worker first reported the synthesis and catalytic application of ruthenium(II) complex (**Figure 2**) containing chiral tetradentate (N_2O_2) Schiff base ligand, and these type of metal complexes have been used in the catalysis application of asymmetric epoxidation of unfunctionalised olefins.

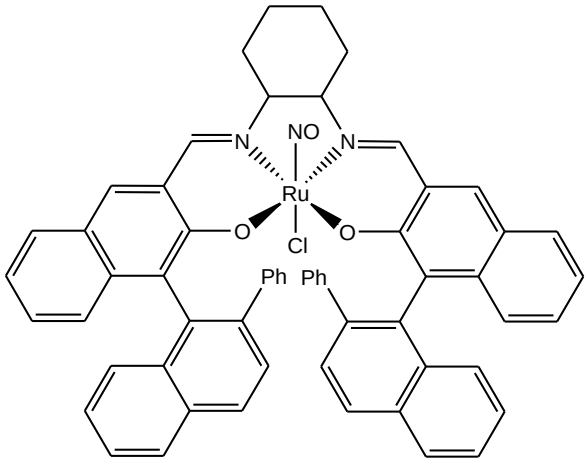


Figure 2: The structure of ruthenium(II) complex reported by Katsuki *et al*. (1999)

In addition, Telfer and Kuroda (2003) and Ding *et al*. (2008) also reported the catalytic properties of the Schiff base complexes (**Figure 3**), which are using salicyladehyde as the starting material. They found that the catalytic properties of the Schiff base complexes can be altered by changes in the Schiff base portion in epoxidation, hydrogenation and miscellaneous reaction.

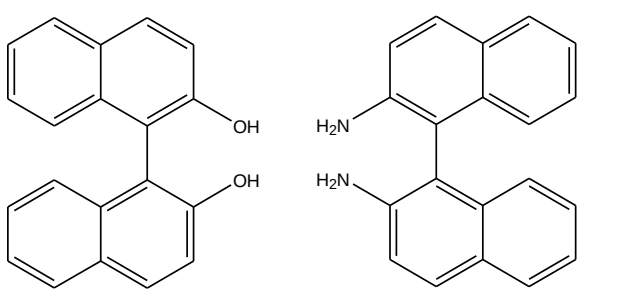
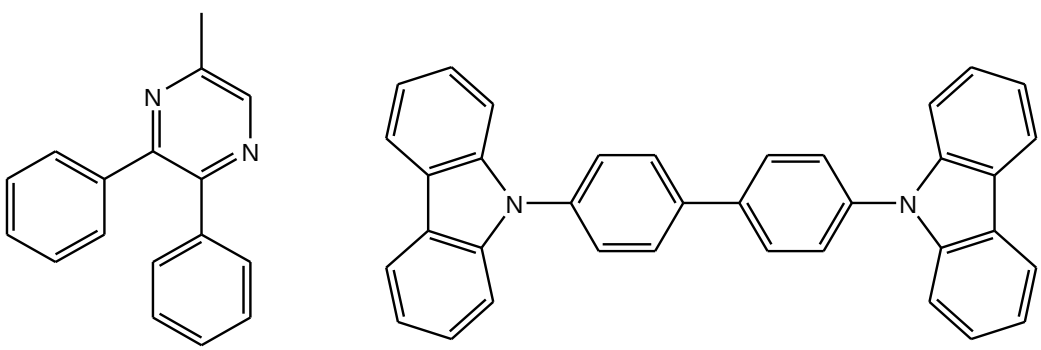


Figure 3: The structure of BINOL and BINAM

In addition, the homogeneous catalytic reaction of transition metal Schiff base complexes was also reported in the catalysis application. For examples, polymer and zeolite encapsulated Schiff base complexes are the most widely used. This is due to its advance catalytic activity in the Heck reaction (Lyer *et al*., 2004).

1.2.2 Luminescent applications

Apart from the catalysis applications, luminescent properties of metal complexes also show different from the simple organic molecules. This is due to the fact that the metal centre, which is a heavy atom, can significantly generate intersystem crossing (ISC) in the excited states of the complex and changing the single excited states to triplet excited states. As a result, the luminescent metal complexes can generate relatively high efficiencies and long life phosphorescence (**Figure 4**) (Zhang *et al*., 2005). These properties have been widely applied in the light emitting devices such as organic light emitting diode (OLED) devices (Baldo *et al*., 1998).



5-Methyl-2,3-diphenyl-pyrazine
(MDPP)

4,4' N,N'-dicarbazole-biphenyl
(CBP)

Figure 4: The structure of MDPP by Zhang *et al*. (2005) and CBP by Baldo *et al*. (1998) act as donor and host material

Furthermore, Dedeian and co-worker (2007) had used *fac*-[Ir(ppy)$_3$] (**Figure 5**) (ppy = 2-phenylpyridine) as prototypical example. The mixing of orbital of the coordination phenylpyridine with valance 5*d* orbital of iridium give a highest occupied molecular orbital (HOMO) with mixed of phenyl and iridium and the other hand the lowest unoccupied molecular orbital (LUMO) showed primarily phenylpyridine based. The structural change of the ligand also can lead to an undesirable reduction where it has a little effect on the energy of emissive $\pi \rightarrow \pi^*$ excited state of the complexes. This was proved by the short luminescence decay times in the study of *fac*-[Ir(ppy)$_3$] (Arm *et al*., 2005). In